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INVESTIGATION OF ALTERNATE PACKAGING FOR DS2

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13. ABSTRACT *(Maximum 200 words)*

Storage containers for DS2 have always been made of metal. Suggestions have been made over the years that plastics be investigated for use as DS2 containers. Past studies indicated that the only plastics suitable for containing DS2 were Teflon®, polyethylene, Kynar® (polyvinylidene fluoride), and PEEK (polyether ether ketone). Commercially available containers made from these materials were used for an extended laboratory storage study. Only Kynar® showed any promise (containers from PEEK were not available). Experimental containers in the M13 Decontaminating Apparatus: Portable, 14-L configuration were manufactured from Kynar® for additional studies. Whereas, the Kynar® itself was determined resistant to DS2, the experimental Kynar® containers themselves did not survive the testing required to certify them as shipping containers for DS2. This failure was probably due to the configuration of the experimental Kynar® containers. Kynar® containers in other configurations should be evaluated. Until these tests can be completed, DS2 will continue to be packaged in metal containers with stainless steel being the preferred material for these containers.

14. SUBJECT TERMS

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PEEK	Plastics	Reactivity	Plastic containers

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PREFACE

The work described in this report was started in October 1990 and completed in December 1992. Data collected during the laboratory studies of plastic containers portion of the project are recorded in laboratory notebook 92-0105.

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INVESTIGATION OF ALTERNATE PACKAGING FOR DS2

1. BACKGROUND

The U.S. Army uses DS2, which was developed in the 1950s,[1] as the standard decontaminant in field situations. It is composed of diethylene triamine (70% by weight), ethylene glycol monomethyl ether (28%), and sodium hydroxide (2%). To maintain reactivity, DS2 must be prepared and packaged under nitrogen. If DS2 is exposed to the atmosphere, it rapidly absorbs carbon dioxide and moisture. Absorption of carbon dioxide causes the DS2 to lose reactivity,[2] and water absorption causes it to become extremely corrosive.[3,4]

Introduction of DS2 into the field began in the 1960s. Packaging for DS2 includes 1-1/3-qt cans (for use with the M11 Decontaminating Apparatus, Portable) and 5-gal pails (for use when large quantities of DS2 are required, such as at an Equipment Decontamination Station as part of Thorough Decontamination operations per Field Manual 3-5, NBC Decontamination[5]). Since 1983, DS2 has also been packaged in a 14-L container that is a component of the M13 Decontaminating Apparatus: Portable, 14 L.

All these packaging configurations are made from carbon steel (either cold rolled or terne plate[6]), which is compatible with DS2,[7,8] provided the containers are kept sealed with the nitrogen in place.[9] These containers must be specially made with welded seams so there is no possibility of air reaching the DS2, because DS2 is corrosive to steel if it is exposed to the atmosphere and picks up moisture as stated above. Because of this, these metal containers are relatively expensive.

It must be noted that the DS2 itself does not corrode carbon steel if kept sealed under nitrogen. Corrosion occurs when the paint film on the containers is damaged and rusting begins at the site of the damaged paint film, causing a hole in the container metal. The DS2 is thus exposed to atmospheric moisture and becomes very corrosive.[3,4] It then attacks the metal as it leaks from the container. If the DS2 contacts any other containers nearby, further leaks result.

To eliminate the corrosion problem and the expense of welded metal containers, many suggestions have been made that DS2 be packaged in plastic containers as are other chemicals. Several studies were conducted by the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC) and its predecessor organizations to investigate plastic materials to determine if any had sufficient resistance to the penetration of DS2 to be used for containers.[10-13] Data from DS2 compatibility studies were also used to select plastics for further study.[14-16] Also, the hazardous waste industry was surveyed to determine the type of plastic containers they use for storing hazardous materials and waste.[17]

Results of the waste industry survey revealed that they normally use polyethylene containers. However, Environmental Protection Agency (EPA) regulations mandate that the waste industry store hazardous liquids for no

longer than 1 yr. As a result, the information is of little use for selecting a plastic to hold DS2 in the inventory where it might sit unused for many years. The other referenced studies showed that the plastics with the best resistance to DS2 penetration were Teflon®, polyethylene, Kynar® (Polyvinylidene Fluoride [PVDF]), and polyether ether ketone (PEEK). No containers made from PEEK could be found commercially, so this material was not tested further. Results of studies performed on containers made of the other three materials are the subject of this report.

2. TEST PROCEDURES AND RESULTS

2.1 Laboratory Studies of Plastic Containers.

Commercial sources of containers made from the materials found to be resistant to DS2, as stated above, were identified and sample containers were obtained. The types of materials and sizes of the test containers are shown in Table 1.

Table 1. Plastic Containers Evaluated

Test Container Designation	Plastic Used in Test Container*	Size of Test Container	Manufacturer
A	Fluorinated Lined HDPE	1 qt	Air Products and Chemicals
B	FEP Teflon®	16 oz	Nalge Co.
C	PFA Teflon®	8 oz	Nalge Co.
D	Fluorinated Lined HDPE	32 oz	Nalge Co.
E	Kynar®	500 mL	MAR-Class Plastic Products, Inc.
F	TPX	32 oz	Nalge Co.
G	Kynar®	5 gal	MAR-Class Plastic Products, Inc.

*HDPE - High Density Polyethylene
FEP - Fluorinated Ethylene-Propylene
PFA - Perfluoro Alkoxy
TPX - Polymethyl Pentene

In October 1990, containers of DS2 were obtained from stock. The containers were opened, and DS2 was transferred to the 7 plastic test containers (Table 1) and 2 glass containers. A pump and Teflon® tubing were used

for the transfer. The DS2 in the glass containers was used as control samples during the course of the study. Containers were filled under a blanket of dry nitrogen, leaving approximately 5% nitrogen headspace in each container. Caps were firmly secured and wrapped with Parafilm®. These were placed in a fume hood in the laboratory (Room C-602, Building E3549 [The Berger Laboratory Complex]). No attempt was made to control the temperature in the room. The samples experienced whatever ambient temperature was in the laboratory. The containers were observed periodically for any changes in appearance. The contents were analyzed at 8 and 25 mo of storage for chloroform reactivity, specific gravity, and viscosity. Physical appearance of the DS2 was also recorded at the time the samples were taken for analysis. Each time samples of DS2 were removed from the containers for analysis, the containers were resealed under a dry nitrogen blanket. Procedures followed to make these analyses were those cited in the DS2 specification, MIL-D-50030H.[18]

2.1.1 Physical Appearance.

Freshly made DS2 is transparent and slightly yellow in color. Physical appearance of the DS2, as determined by visual observation of the material in each of the test containers, was recorded after 8 and 25 mo of laboratory storage. Changes in the condition of the containers were also noted. Results of this visual examination are shown in Table 2.

2.1.2 Chloroform Reactivity.

Chloroform reactivity is one of the main tests used to determine if DS2 is still reactive. The minimum acceptable value for chloroform reactivity shown in the DS2 specification (MIL-D-50030) is 350 mg.[18] Measurement of chloroform reactivity was by a Volhard titration method. Chemicals used in the analysis were nitric acid, ferric ammonium sulfate, silver nitrate, and nitrobenzene. Potassium thiocyanate was the titration liquid. Starch was used as an indicator of the endpoint. Duplicate determinations were made for each sample. Chloroform reactivity of the samples in the plastic containers was measured after 8 and 25 mo of storage. Values obtained are shown in Table 3.

2.1.3 Specific Gravity.

The specification for DS2[18] requires that the specific gravity be between 0.970 and 0.980 measured at 25 °C. Specific gravity measurements were made in accordance with ASTM D 891-89 (as stated in MIL-D-50030). A calibrated dilatometer, identified on the instrument as K-17, was used to make the measurements. The equation used to calculate the volume of a given quantity of material was

$$\text{Volume (mL)} = 52.59 + 0.2044R$$

where R is the reading on the neck of the dilatometer. Measurements were made at 25 °C. Only single determinations were made for each sample.

Table 2. Physical Appearance of DS2 and Containers After Storage at Ambient Conditions

Test Container Designation	Plastic Used in Test Container*	Visual Observations	
		8 mo	25 mo
A	Fluorinated lined HDPE	DS2 in the container had small gel bodies in the liquid	DS2 in the container had small gel bodies in the liquid
B	FEP Teflon®	No apparent changes	Gelling was present throughout the DS2. The DS2 was a dark honey color. The container had a permanent indentation in the bottle wall near the top.
C	PFA Teflon®	Darker in color than other samples	No gelling present although the DS2 was a very dark honey color. This container also had a permanent indentation in the bottle wall near the top.
D	Fluorinated Lined HDPE	No apparent changes	No gelling; no color change
E	Kynar®	No apparent changes	A very small crack on the side of the lid
F	TPX	Gelling throughout the sample	Slight gelling in the DS2, gelled precipitation on the bottom of the bottle, small white flakes present on the sides of the bottle.

Table 2. Physical Appearance of DS2 and Containers After Storage at Ambient Conditions (Continued)

Test Container Designation	Plastic Used in Test Container*	Visual Observations	
		8 mo	25 mo
G	Kynar®	No apparent changes	No gelling noted. The container interior was permanently discolored.
Controls	Glass	No apparent changes	No gelling.

*HDPE - High Density Polyethylene
FEP - Fluorinated Ethylene-Propylene
PFA - Perfluoro Alkoxy
TPX - Polymethyl Pentene

Table 3. Chloroform Reactivity of Stored DS2 Samples

Test Container Designation	Plastic Used in Test Container*	Amount of Chloroform Destroyed 8 mo		25 mo	
		mg		mg	
A	Fluorinated lined HDPE	353.1	351.1	337.2	339.2
B	FEP Teflon®	341.1	339.1	320.4	321.2
C	PFA Teflon®	323.2	319.2	225.4	232.2
D	Fluorinated lined HDPE	352.1	351.1	355.1	359.1
E	Kynar®	354.1	351.1	345.1	345.1
F	TPX	315.2	317.2	231.4	215.5
G	Kynar®	349.5	352.9	345.1	349.1
Control 1	Glass	349.1	348.3	349.1	355.1
Control 2	Glass	350.3	353.1	352.7	355.1

*HDPE - High Density Polyethylene
FEP - Fluorinated Ethylene-Propylene
PFA - Perfluoro Alkoxy
TPX - Polymethyl Pentene

A specific gravity determination was attempted at -30 °C to be used as a comparison with the determinations performed at 25 °C. But as the DS2-filled dilatometer was placed into the cold bath, the volume contracted below the graduations on the neck. This prevented an accurate volume from being measured. Values obtained for the stored samples are shown in Table 4. As noted in the table, measurements were made only after 8 mo of storage.

2.1.4 <u>Viscosity</u>.

Once exposed to the atmosphere, DS2 degradation is initiated and eventually, if degraded far enough, the DS2 begins to thicken. It then becomes unusable in either the M11 or M13 portable decontaminating apparatuses. The acceptable value for DS2 viscosity shown in the specification[18] is 420 cP maximum measured at -30 °C. Viscosity determinations were conducted in accordance with ASTM D 445-88, as required by the DS2 specification. A calibrated viscometer (No. 400 X516) was used to determine the efflux times. Kinematic viscosity was determined by multiplying the flow time in seconds, by the calibration constant of 1.306 cSt/s. Absolute viscosity in centipoise (cP) was obtained by multiplying the kinematic viscosity at -30 °C by the specific gravity determined at 25 °C. Values measured on the stored samples are shown in Table 5. As noted in the table,

Table 4. Specific Gravity of Stored DS2 Samples Measured at 25 °C

Test Container Designation	Plastic Used in Test Container*	Specific Gravity 8 mo
A	Fluorinated lined HDPE	0.9708
B	FEP Teflon®	0.9721
C	PFA Teflon®	0.9720
D	Fluorinated lined HDPE	0.9701
E	Kynar®	0.9704
F	TPX	0.9749
G	Kynar®	0.9698
Control 1	Glass	0.9696
Control 2	Glass	0.9696

*HDPE - High Density Polyethylene
FEP - Fluorinated Ethylene-Propylene
PFA - Perfluoro Alkoxy
TPX - Polymethyl Pentene

values were not measured for container B at 25 mo. Per the comments in Table 1 for container B, there was so much gelling of container B contents that a viscosity measurement could not be made. For container F, only one reading was made at 8 mo. Again as shown in the comments in Table 1, the DS2 in container F had gelling throughout the sample, which made the viscosity very high, 1713 cP. Because the viscosity was so high due to gelling, a second measurement was not made. After 25 mo of storage, the viscosity of the DS2 in container F had dropped to 701 cP. This was due to precipitation of the gel bodies (see comments in Table 1). Even though the viscosity had dropped, it was still too high for container F to be considered an acceptable DS2 storage container.

2.2 Containers of Polyvinylidene Fluoride (PVFD).

2.2.1 Container Production.*

Late in 1990, All-Bann Enterprises, Inc. (Anaheim, CA) which was manufacturing black, polyethylene containers to be used as a training container for the M13 Decontaminating Apparatus: Portable, 14 L, was

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*Decontamination Solution, Number 2 (DS2) Polyvinylidene Fluoride (PVDF) Container, All-Bann Enterprises, Inc., Anaheim, CA, 17 May 1991, unpublished data.

Table 5. Viscosity of Stored DS2 Samples Measured at -30 °C

Test Container Designation	Plastic Used in Test Container[a]	Viscosity 8 mo		Viscosity 25 mo	
		cP		cP	
A	Fluorinated lined HDPE	334.6	332.7	356.2	355.7
B	FEP Teflon®	382.5	389.1	[b]	
C	PFA Teflon®	631.6	645.8	607.3	610.6
D	Fluorinated lined HDPE	322.2	314.2	330.9	330.4
E	Kynar®	336.7	329.7	380.9	379.4
F	TPX	1713.0[c]	[d]	701.7	701.9
G	Kynar®	320.2	321.8	334.4	335.4
Control 1	Glass	317.4	323.5	343.2	343.3
Control 2	Glass	339.1	336.9	332.7	335.8

[a]HDPE - High Density Polyethylene
FEP - Fluorinated Ethylene-Propylene
PFA - Perfluoro Alkoxy
TPX - Polymethyl Pentene
[b]Measurements not made because of excessive gelling of the samples.
[c]Measurement was extremely high because of large gel particles in the solution prevented proper flow in the viscometer.
[d]Only measurement made because the large gel bodies in the DS2 did not easily flow through the viscometer.

requested to attempt to manufacture containers in the same configuration from Kynar®. These containers were to be tested to determine if they would meet the requirements for storing and transporting DS2. Rotational and blow molding were considered for manufacturing the containers. Both processes investigated could produce containers to the general configuration required. Modifications to the design would have been required to produce the container using the rotational molding process, and the rotational molding process is not generally used in high volume production. Blow molding is the process currently used to produce the M13 black plastic containers. Based on investigation of available data from suppliers of PVDF, blow molding was selected as the process to be used to produce the desired containers for test.

The PVDF selected for production of the test containers was manufactured by Solvay Polymers, Inc. (Houston, TX) under the trade name Solef. The specific material used was Solef 1010/0001, which is the extrusion grade

material supplied by Solvay. Solef 1010/0001 conforms to ASTM D 3222-88 and is designated as a Type II resin per paragraph 3.31 of this standard.

The Government requested that the test containers be green in color conforming to 34082-34094 of Federal Standard 595. Pigment for the PVDF was specially compounded by Color Science (Santa Ana, CA) with an ordering number of CS1G054V. Each 100 lb of Solef 1010/0001 required 409 g of pigment. The pigment was supplied in powder form and mixed intimately with the Solef 1010/0001 by rotational blending before processing.

Four production runs were performed to establish the processing parameters for producing the containers. The primary objective of the first run was to establish heat requirements and determine if the flow characteristics would require any mold modifications. It was determined that no mold modifications would be needed. The containers produced during this run were contaminated with polyethylene that had remained in the transfer area between the extruder barrel and the accumulator. Common practice in the blow molding industry is to continue running material until all the previous material would be purged from the equipment. Due to the cost of PVDF, this was impractical. Therefore, the equipment was shut down and completely disassembled and cleaned. All material that ran through the machine during this first run (approximately 650 lb) was scrapped.

The second production run yielded containers with the overall configuration desired. To achieve the desired cross section in the corner areas, the overall weight had to be increased to over 8 lb and the wall sections in the side areas were in excess of 0.250 in. This thickness was not acceptable. The heavy wall section would limit the liquid capacity of the container. Furthermore, the units had an unacceptable gloss. Fourteen containers were produced during this run; two were provided to the Government. The remaining containers were ground up for use in further production.

Prior to production run 3, additional Solef 1010/0001 had to be procured due to the contamination during run 1 and normal material losses during runs 1 and 2. During run 3, it was noticed that the material was burned. The blow molding machine was again disassembled and cleaned. All containers produced during this run (approximately 450 lb) were scrapped.

The final production run was successful and produced 37 containers. The containers were numbered serially from 301 through 337. Approximately 120 lb of material in regrind form remained at the end of production of the containers.

2.2.2 Container Evaluations.

All-Bann provided containers numbered 336 and 337 to Hauser Chemical Research, Inc., (Boulder, CO) to be tested for effects of exposure to DS2. Tests performed included absorption of DS2 by the PVDF container material, permeation of DS2 through the PVDF container material, tensile strength and percent elongation before and after exposure to DS2, and effect of PVDF on DS2 reactivity. The remainder of the containers were provided to the Government. Of these, nine (numbers 301-308 and 311) were sent to the U.S. Army Materiel

Command Packaging, Storage, and Containerization Center (Tobyhanna, PA) for performance oriented packaging testing and 12 (numbers 310, 312, 314-316, 319, 321-325, and 329) were subjected to a rough handling test performed by the Test and Evaluation Office, Research, Development and Engineering Support Directorate, U.S. Army Chemical Research, Development and Engineering Center.

2.2.2.1 Effects From Exposure to DS2.*

- DS2 Absorption by PVDF Material. The two containers from the 37 produced, which were furnished to Hauser Chemical Research, Inc., by All-Bann Enterprises, Inc., were cut into sections to be used for various tests. Absorption of DS2 by the PVDF base material was determined by weight change of the container bodies samples immersed in DS2. Measurements were made at 7, 30, 60, and 90 days. Data obtained are shown in Table 6. Based on the data collected, PVDF did not appear to absorb DS2.

Table 6. Absorption of DS2 by Polyvinylidene Fluoride as Determined by Immersion Testing at 70 °C*

Exposure Time	Sample 1 Weight	Sample 1 Change		Sample 2 Weight	Sample 2 Change	
days	g	g	%	g	g	%
0	6.8821			6.5164		
7	6.8820	0.0001		6.5174	0.0010	
30	6.8795	-0.0026	-0.04	6.5150	-0.0014	-0.02
60	6.8775	-0.0046	-0.07	6.5135	-0.0029	-0.04
90	6.8755	-0.0066	-0.10	6.5113	-0.0051	-0.08

- Permeability of the PVDF to DS2. Permeability was measured using a vented permeation cell. The tests were run at 70 ± 5 °C. Portions of the containers cut up for the absorption test were used for this test. The samples were "remolded" into flat plaques 0.090 in thick. The samples used for the test were 15.2 cm^2 in area. Air used to vent the underside of the plastic in the permeation cell was analyzed for the presence of DETA and EGME by gas chromatograph (GC). Detection limit of the GC for DETA was 1.3 μg and for EGME was 44 μg. Permeability was measured at 7, 30, 60, and 90 days. No detectable amounts of DS2 (using analysis for DETA and EGME) were found in either sample.

*Decontamination Solution, Number 2 (DS2) Polyvinylidene Fluoride (PVDF) Container, All-Bann Enterprises, Inc., Anaheim, CA, 17 May 1991, unpublished data.

● Tensile Properties of PVDF Exposed to DS2. Tensile strength of samples of the PVDF containers was measured according to the procedures in ASTM D638. Two samples from each container were used for the testing. Yield strength, strength at fracture, and elongation at fracture were measured before and after exposure to DS2. Exposure time was 90 days at 70 ± 5 °C. Results from the test are shown in Table 7. These data show that there was an increase in the strength at fracture of the PVDF as a result of exposure to DS2, whereas the percentage elongation at fracture decreased by 50%.

Table 7. Effects of DS2 on the Tensile Strength of Polyvinylidene Fluoride*

Sample Condition	Yield Strength	Sample 1 Strength At Fracture	Elongation At Fracture	Yield Strength	Sample 2 Strength At Fracture	Elongation At Fracture
	psi	psi	%	psi	psi	%
Unexposed	7420	4820	15.0	7450	4810	17.5
	7530	4160	20.0	7390	3680	20.0
Exposed	7850	7610	7.5	7250	6750	10.0
	8120	7550	7.5	7470	6940	10.0

● Effect of PVDF on DS2 Chloroform Reactivity. Chloroform reactivity was measured using the procedures set forth in the DS2 specification.[18] Measurements were made before and after 90 days of contact with PVDF samples. Hauser reported that their first analysis per the specification did not have a clear end point when the solution was back-titrated with potassium thiosulfate. The silver nitrate and potassium thiosulfate used were 0.1 N instead of the 0.025 N specified. Precision of the titration was estimated at ±3%. Consequently, a second set of analyses was performed using 0.025 N solutions as called for by the specification. There was some question regarding the end point of the titration; so titration volumes were noted at the beginning and end of the color change leading to a range of chloroform reactivities. Results of both sets of titrations performed using the two procedures are shown in Table 8. There was no decrease in chloroform reactivity of the DS2 exposed to the PVDF.

*Decontamination Solution, Number 2 (DS2) Polyvinylidene Fluoride (PVDF) Container, All-Bann Enterprises, Inc., Anaheim, CA, 17 May 1991, unpublished data.

Table 8. Effect on Chloroform Reactivity of DS2 by Exposure to Polyvinylidene Fluoride*

Sample	Amount of Chloroform Destroyed (mg)
Set 1	
Reference, open 90 days	349
1 90 days exposure	347
2 90 days exposure	399
Set 2	
Reference, freshly opened	366 369-376 373-377
Reference, open 90 days	353-390 355-357
1 90 days exposure	388-390 385-387
2 90 days exposure	393-395 390-392

2.2.2.2 Performance Oriented Packaging.**

The U.S. Army Materiel Command Packaging, Storage, and Containerization Center conducted Performance Oriented Packaging Testing on the PVDF containers. In accordance with United Nations (UN) recommendations, the containers should have been conditioned with DS2 for 180 days before performance testing. It was understood that if this initial testing was successful, conditioned testing would be required before the containers could be certified for fielding.

*Decontamination Solution, Number 2 (DS2) Polyvinylidene Fluoride (PVDF) Container, All-Bann Enterprises, Inc., Anaheim, CA, 17 May 1991, unpublished data.

**Performance Oriented Packaging Testing of a Developmental Jerrican for Decontaminating Agent DS2 - Packing Groups I and II, DODPOPHM/AYP/TR91072, U.S. Army Materiel Command Packaging, Storage, and Containerization Center, Tobyhanna, PA, 21 August 1991, unpublished data.

The containers were tested bare (i.e., with no packaging). Testing in this manner provides flexibility for shipping the item with regard for the level of packaging and packing. If the container were to be tested inside a fiberboard box, it then becomes an inner container in combination packaging. Absorbent material would be required and combination packaging restrictions would apply.

Previous testing of DS2 containers was conducted according to Packing Group I and II test parameters. Therefore, because the container is developmental in nature, test parameters for Packing Group I were used. If there was failure at the Packing Group I level, then testing would be repeated using the parameters for Packing Group II.

In conducting the drop test, initially all five drops were to be performed on the same container (five drops total) with three replications. Five drops per packaging exceed UN and ASTM recommendations (i.e., one drop on a side or corner per container) and is in accordance with DoD policy issued by the Office of the Assistant Secretary of Defense. For the drop test, a free fall drop leaf table, initially set for 6 ft, was used. The impact surface was the 3/4-in. steel impact plate of the table, resting in turn on a 3-in. steel plate, imbedded in 4 ft of concrete. The table was reset for 4 ft for Packing Group II testing. The test specimens had been conditioned for 72 hr at -4 °F. The first drop orientation from 6 ft was diagonally onto the top edge of cold conditioned container number 304. A portion of the handle broke off the container. There was no leakage, because the portion of the handle that broke was solid plastic. The second drop orientation was flat onto the short side having the outlet plug assembly. The adjacent side shattered, and the bottom was broken around the "edge." In accordance with the test plan, the flat side drop was repeated on container number 305 from 4 ft. The handle split near the position where the handle met the top of the container. There was leakage of the test liquid. Because there was failure, no further drop testing was conducted.

For the stack test, a compression tester was not used because it would not hold the load constant for the required 28-day time required for the test. To simulate a stacked load for transportation and storage, a 500-lb steel plate and assorted weights were placed on top of the test packagings, distributing the test load over the three test specimens. The total top load was 230 lb/test specimen. Testing was conducted at 104 °F. Test containers 303, 307, and 308 maintained the test weight for the required 28-day time in a 104 °F environment. Even though the stacking weight exceeded the minimum recommended, there was no damage, leakage, or rupture noted; also, there was no deflection detected.

The leakproofness and hydraulic pressure tests were conducted because the single packaging is intended for the containment of liquids. The minimum hydraulic test pressure for Packing Group I was chosen because there was no value available for vapor pressure of DS2. Metal containers for DS2 have demonstrated the capability to maintain the 36 psi internal pressure designated for Packing Group I. A compressed air valve was threaded into the plug assembly of the test PVDF container. There was leakage upon initial pressurization of test container number 311. Application of Teflon® tape

around both threaded fittings was sufficient to prevent leakage. Once the container was pressurized to 4.4 psi and maintained for 10 min, there was no leakage noted. At approximately 30 psi, there was leakage noted from the gasket areas underneath the plug assembly of container number 311. Due to the leakage, the test was concluded before the desired 36 psi was reached.

The vibration test was performed to determine if the container would meet U.S. Department of Transportation requirements for domestic shipping. A single water-filled container, number 301, was tested in accordance with ASTM D999, Method A1, Repetitive Shock Test, on a vibration table for 1 hr at 4.3 Hz. No leakage, rupture, or damage to the container was noted.

2.2.2.3 Rough Handling Test.*

This test was performed to supplement the Performance Oriented Packaging tests and determine if containers produced from PVDF could withstand the rough handling which they might encounter during field use. Twelve containers were tested. Two underwent a drop test at ambient conditions; ten, of the which five were preconditioned at 160 °F and five were preconditioned at -50 °F, were subjected to loose cargo testing. Once the 10 containers had completed loose cargo testing, they were also subjected to the drop test. Those preconditioned at -50 °F were further subdivided, where one was dropped at -50 °F, one at -28 °F, one at 0 °F, and two at 30 °F. Visual checks were made on the containers after each test. The containers tested at hot and ambient conditions were filled with water. Those containers tested at the other temperatures were filled with a mixture of 2:1 ethylene glycol:water. At the conclusion of the tests, each item was inspected visually for damage and leakage. If there was no visible leakage of the liquid or cracks in the container that would permit leakage, the item was considered as having passed the test.

Loose cargo vibration testing on containers, conditioned as described above, was performed according to FED-STD-101C, Method 5019.1. The containers were tested without packaging. All orientations were tested with the exception that no container was tested on the top surface. Thus, for 2 1/2 hr, five orientations were tested at 30 min each. None of the test items showed any degradation or leakage as a result of testing following the procedures specified; thus all containers passed the loose cargo rough handling at the temperature extremes.

Drop testing of conditioned items was performed according to the transit drop test as described in MIL-STD-810E, Method 516.4, Shock, Procedure IV, Transit Drop (without transit case), Table 516.4-II (48 in., 26 drops). The 26 drops were divided among the five items in hot conditioning and among the five items in cold conditioning. When the first few drops severely damaged the test item, the test director suspended testing. The order in which the 26 drops were performed on the five containers is shown in

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*Test Report for Rough Handling Test of DS2 Kynar Container, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

Table 9. Drop Test Matrix Showing Container Orientation During the Drop Test*

Container	Drop Sequence**
1	Bottom; Edge (BF:RS); Left Side; Edge (RS:FF); Edge (T:FF)
2	Edge (LS:BF); Corner (RS:BF:B); Edge (B:FF); Corner (T:RS:BF); Top
3	Edge (B:RS); Corner (LS:BF:B); Right Side; Edge (B:LS); Edge (T:LS); Corner (T:LS)
4	Corner (B:LS:FF); Edge (B:BF); Front Face; Edge (T:RS); Corner (T:LS:FF)
5	Edge (LS:FF); Corner (B:RS:FF); Back Face; Edge (T:BF); Corner (T:FF:RS)

**Orientations were with the container upright and the quick disconnect fitting facing forward.

T - Top   FF - Front Face
BF - Back Face   RS - Right Side
LS - Left Side   B - Bottom

Edge (RS:FF) represents the edge between the right side and the front face.

Corner (LS:BF:B) represents the corner intersecting the left side, the back face, and the bottom.

*<u>Test Report for Rough Handling Test of DS2 Kynar Container</u>, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

the test matrix in Table 9. Data for items dropped at ambient temperature are in Table 10. Data for containers conditioned at 160 °F are in Table 11. Data for the -50 °F containers are in Table 12. Because of the containers failure at -50 °F, the other containers were reconditioned at -28 °F to investigate the criteria of basic cold climatic design type. Instead of overnight conditioning, a period of 5 hr was used. A thermocouple was placed in the interior of one of the containers before dropping to verify conditioning. A reading of -30 °F was recorded which falls inside the ±3.6 °F tolerance allowed in MIL-STD-810E. Results of these tests are shown in Table 13. Again, severe failure was noted. The remaining three containers were thus reconditioned at 0 °F to investigate the point where the containers were not

Table 10. Drop Test Results* for Containers At Ambient Temperature

Container	Drop Orientation	Results
329	Bottom	No damage.
	Back face/bottom edge	No damage.
	Front face/bottom left Corner	A split in the plastic at the outlet plug from a secondary hit of the outlet plug against the dropping apparatus.
	Top/front face edge	No further damage.
	Top	Total breakage of plastic around the outlet plug, with the plug going into the container.
324	Bottom/right side edge	No damage.
	Right side	No damage.
	Back face/right side edge	No damage.
	Top/left side/front face	Cracked on high part of container (left side) and dented.
	Top	Plastic cracked through where outlet plug assembly attaches to container. Unrelated to previous crack.

*Test Report for Rough Handling Test of DS2 Kynar Container, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

Table 11. Drop Test Results* for Containers Conditioned to 160 °F

Container	Drop Orientation	Results
319	Bottom	No damage.
	Back face/right side edge	No damage.
	Left side	No damage.
	Right side/front face edge	No damage.
	Top/front face edge	Small leak at interface where outlet plug mounts into container. Deep dent in top/left side front corner (high area).
325	Left side/back face edge	No damage.
	Right side/back face/bottom corner	No damage.
	Bottom/front face	No damage.
	Top/right side/back face corner	Small leak at interface where outlet plug mounts into container. Moderate dent in top corner (high area).
	Top	Same as previous drop.
322	Bottom/right side edge	No damage.
	Left side/back face/bottom corner	No damage.
	Right side	No damage.
	Bottom/left side edge	No damage.
	Top/left side edge	Small leak at interface where outlet plug mounts into container. Deep dent in top/left side front corner (high area).
	Top/left side/back face corner	Same as previous drop.

Table 11. Drop Test Results* for Containers Conditioned to 160 °F (Continued)

Container	Drop Orientation	Results
323	Bottom/left side/front face corner	No damage.
	Bottom/back face edge	Small leak on bottom. Crack follows along the length where the bottom starts to recess on left side, bottom edge.
	Front face	Not done.
	Top/right side edge	Not done.
	Top/left side/front face corner	Not done.
321	Left side/front face	No damage.
	Bottom/right side/front face	No damage.
	Back face	No damage.
	Top/back face edge	Handle broke in two places; near base and on horizontal part near base. Hollow inside handle, about 1/4 in. long by 1/8 in. wide.
	Top/front face/right corner	Small leak at interface where outlet plug mounts into container. Deep dent in top/right side front corner (high area).

*Test Report for Rough Handling Test of DS2 Kynar Container, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

Table 12. Drop Test Results* for Containers Conditioned to -50 °F

Container	Drop Orientation	Results
312	Bottom	Two large pieces blew out from the container. One piece (5" x 10") was from the bottom/right front corner. The other piece (5.5" x 8") was from the bottom right side running adjacent to the other piece to the back corner. Thickness of the plastic was uneven; going from 3/32 to 3/8 in. at the bottom/right front corner. The bottom/back corner was as little as 1/16 in. thick. However, the cracking did not seem to be preferential to the thickness of the material.

Note: Because of the severe damage during this first drop, no additional drop orientations were performed at this temperature.

Table 13. Drop Test Results* for Containers Conditioned to -30 °F

Container	Drop Orientation	Results
315	Bottom	No damage.
	Back face/right side edge (drop was actually more on back face)	No damage.
	Left side	Fracture of the right side and back face. Three vertical cracks, all starting from the bottom: 6.5 in. crack from the bottom/right front corner; 10.5 in. crack right of center on the right face; and 8 in. crack up the back face. Two horizontal cracks: a jagged 5 in crack in the middle of the right face; a total fracture of the right side/bottom edge with the bottom/right side back corner missing. Variable thickness of material in the container.

Note: Because of the damage noted after the third drop, no additional drop orientations were performed at this temperature.

*<u>Test Report for Rough Handling Test of DS2 Kynar Container</u>, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

so brittle as to break open completely. Results for containers conditioned to 0 °F are in Table 14. As before, failure was noted. The remaining two containers were conditioned to 30 °F to try and reduce brittleness of the plastic. Table 15 lists the results of drops performed on containers conditioned to 30 °F. No containers survived the required cold temperature testing.

2.3 Modifications to Present Metal Containers.

Because the work with available plastic materials and molds did not produce a container that could be used for shipping and storing DS2, attention was directed toward actions that could be taken to improve on the present container. Thicker carbon steel containers, stainless steel containers, use of a zinc-rich primer to deter rusting of carbon steel containers, and changes in manufacturing techniques to reduce the locations where containers can corrode were investigated under this effort.

The entire program was performed under contract.[19] Salt fog and cyclic storage testing were included in the evaluations. The salt fog test was used to determine if any of the alternatives produced a container with better corrosion resistance than the current container. The cyclic storage test was performed to determine how effective the proposed container configurations would be for use in storing DS2, and in the future, use in storing DS2P under various climatic conditions.

After the salt fog test, heavy corrosion was observed on all test configurations except the stainless steel containers. As a result of the cyclic storage tests, four containers also failed (developed leaks). These containers were all 1 1/3-qt stainless steel containers, and the leaks all occurred at the seam of the solder cup.[19] Overall the stainless steel containers performed better than the other test configurations.

3. DISCUSSION

3.1 Plastic Containers.

Of the plastic containers tested in the laboratory, only those manufactured from Kynar® (Polyvinylidene Fluoride) demonstrated any ability to hold DS2 for extended periods of time (up to 25 mo in this testing). Data from testing on the stored materials showed a slight increase in the tensile properties of the PVDF as a result of contact with DS2, and the percentage elongation of PVDF decreased by 50%. Containers produced of PVDF to the M13 fluid container configuration were able to withstand a stack test load of 230 lb for 28 days at 104 °F and loose cargo vibration testing. However, they could not pass the pressurization test to 36 psi and the drop test from heights of 4 and 6 ft at temperatures lower than 30 °F.

Note that even before testing on PVDF containers was initiated, we knew that the M13 configuration was not the optimal configuration to be used as a shipping container manufactured from plastic. This knowledge was based on test results of the M13 plastic training container performed during its

Table 14. Drop Test Results* for Containers Conditioned to 0 °F

Container	Drop Orientation	Results
310	Bottom	No damage.
	Back face/right side edge	Fracture of the right side. A 12 in. vertical crack from the bottom/right side back corner up the right side and a horizontal crack that ran from the vertical crack through the right side, front face, and to the middle of the left side. A piece (2 in. x 3 in.) popped out at the intersection of the vertical and horizontal cracks. Thickness of the piece was about 3/16 in.

Note: Because of the damage noted after the second drop, no additional drop orientations were performed at this temperature.

*Test Report for Rough Handling Test of DS2 Kynar Container, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

Table 15. Drop Test Results* for Containers Conditioned to 30 °F

Container	Drop Orientation	Results
316	Bottom	No damage.
	Back face/right side edge	No damage.
	Left side	No damage.
	Right side/front face edge	No damage.
	Top/front face edge	Crack starting at about 10 o'clock around the outlet plug assembly up to the vent port.
314	Bottom/right side edge (landed more on bottom)	No damage.
	Left side/back face/ bottom corner	One long crack going from the top/left side front corner through the outlet plug assembly (which fell into the container) and looping around through the middle of the right side and back through the front face (about 5 in. above the bottom).

*Test Report for Rough Handling Test of DS2 Kynar Container, Test and Evaluation Office, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1991, unpublished data.

contractor development. However, because M13 container molds were already in existence and Kynar® could be used in these molds, the M13 configuration was used to save time in producing Kynar® containers for testing. This does not mean that Kynar® containers in other configurations would also be unable to withstand the types of tests performed on the M13 configuration Kynar® containers. These were just not evaluated due to time and cost constraints. So based on the data collected, PVDF containers (at least in the M13 plastic training container configuration) were dropped from any further consideration in these studies.

3.2 Metal Containers.

Of the variations on the current standard metal container tested, only stainless steel containers passed the salt fog and cyclic storage tests. Detailed results of the testing are found in a previously published report.[19] Thus, stainless steel provides the best configuration of a metal container to be used for packaging DS2.

4. RECOMMENDATIONS

It is recommended that metal containers continue to be used as storage and shipping containers for DS2, and that stainless steel be the metal of choice for these containers. Long term storage tests should be performed on stainless steel containers to determine their ability to contain DS2 for extended periods of time and to measure the stability of DS2 in such containers. Evaluations of other configurations of Kynar® containers should be performed to determine if they will meet the requirements for certification as DS2 shipping and storage containers. Further investigations should continue to find plastic materials for potential use as storage containers for DS2. As the packaging industry is continually improving and new plastics are developed, some material may be found in the future that could prove suitable for holding DS2 for extended periods and also have the low temperature properties needed to pass the packaging tests required.

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